Effective removal of zinc (II) from aqueous solutions by tricalcium aluminate (C_3A)

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Abstract

Recently, studies have identified high zinc levels in various environmental resources, and excessive intake of zinc has long been considered to be harmful to human health. The aim of this research was to investigate the effectiveness of tricalcium aluminate (C_3A) as a removal agent of zinc from aqueous solution. Inductively coupled plasma-atomic emission spectrometer (ICP-AES), X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used to characterize such removal behavior. The effects of various factors such as pH influence, temperature and contact time were investigated. The adsorption capacity of C_3A for Zn^{2+} was computed to be up to 13.73 $mmol \cdot g^{-1}$, and the highest zinc removal capacity was obtained when the initial pH of $Zn(NO_3)_2$ solution was between 6.0 to 7.0, with temperature around 308 K. The XRD analysis showed that the resultant products were ZnAl-LDHs. Combined with the analysis of solution component, it was proved the existence of both precipitation and cation exchange in the removal process. From the experimental results, it was clear that C_3A could be potentially used as a cost-effective material for the removal of zinc in aqueous environment.

Keywords: Zinc, Removal, Tricalcium aluminate (C_3A), Cation exchange, Precipitation

1. Introduction

Aqueous environment pollution caused by excessive zinc emission from zinc manufacturing and other industries known as galvanizing, paints and pigments [1], has gradually drawn more attention from the public and the researchers. Despite of its positive biological functions, high level of zinc is proved to have detrimental effects on human health. Excessive intake of zinc could result in irritability, muscular stiffness, growth retardation, gastrointestinal distress, lung disorders and even cancer [2-4]. Therefore, development of methods to purify water resources against heavy zinc solutes has become very essential.

Currently, various techniques have been used for zinc removal from effluent. Such techniques include chemical precipitation, ion-exchange, adsorption and electrochemical methods [5-8]. Among them, adsorption is considered as one of the most popular and efficient measures due to its simplicity and low energy requirement [9]. Several kinds of adsorbents such as activated carbons [10], kaolin clay mineral [11], biomaterials [12, 13] and layered double hydroxides (LDHs) [14] have been trialed for the removal of zinc. In recent years, LDHs' high adsorption properties and potential industrial applications also made them a viable option. LDHs are a class of layered compounds derived from the structure of mineral brucite, and most can be nominally expressed as a chemical formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A_{x/n}\cdot yH_2O$. M^{2+} and M^{3+} are divalent and trivalent metal cations, and A^{n-} denotes the interlayer anions [15]. Generally, LDHs are able to remove heavy metal ions by two mechanisms: cation exchange and chemical precipitation [14, 16]. In the case of cation exchange, Komarneni et al. postulated that the principal mechanism of heavy metal ions uptake is substitution of M^{2+} ions in the layers of LDHs, through a process known as diadochy [17]. The cation diadochy order of LDHs is $Ca^{2+}<<Mg^{2+}<Mn^{2+}<Cd^{2+}<Ni^{2+}<Co^{2+}<Fe^{2+}<Zn^{2+}$ [18], and Ca^{2+} or Mg^{2+} on the layers of LDHs could be easily exchanged by cations such as Co^{2+}, Fe^{2+} and Zn^{2+}. Moreover, the dissolution of LDHs leads to an increase in pH from 7.0 to more than 9.0 [19], and results in precipitation of metal hydroxides, which is another way to remove heavy metal ions. For example, Co^{2+} and Zn^{2+} removed by MgAl-LDHs were produced by

substitution of the Mg^{2+} on the layers [17]. CaAl-LDH was reported to uptake Zn^{2+} by precipitation process between Zn^{2+} and $Al(OH)_4^-$, which finally formed ZnAl-LDH [20].

Tricalcium aluminate, $Ca_3Al_2O_6$ (C_3A) is an important constituent in cement. It accounts for 5-10% of the clinker mass of ordinary Portland cement (OPC). Tricalcium aluminate can be easily synthesized, and is normally found in discarded concrete. During its hydration process, layered phases $4CaO{\cdot}Al_2O_3{\cdot}19H_2O$ (C_4AH_{19}), $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ (C_4AH_{13}) or $2CaO{\cdot}Al_2O_3{\cdot}8H_2O$ (C_2AH_8) which belong to the family of CaAl-LDHs are initially formed as metastable compounds [21]. The structures of these hydrates [$Ca_2Al(OH)_6^+$] consist of main layers with OH^- anions, and H_2O molecules in the interlayer region. Moreover, Ca^{2+} and $Al(OH)_4^-$ are produced during the hydration process of C_3A, which leads to an increase of pH (approx. 11.8) [22]. Prior works have explored the removal effects of methylorange [23] and Na-dodecylbenzenesulfate [24] by C_3A, and it was quite different from other mechanisms, where LDHs (e.g. MgAl-LDH) were applied directly. It was proved that methylorange was removed by C_3A. The substitution of hydroxyl ions in the interlayer of C_4AH_{19} was involved in the process, and Na-dodecylbenzenesulfate was intercalated into the hydrates of C_3A successfully. CaAl-SDBS-LDH was formed subsequently. However, the feasibility of C_3A for cation removal has yet to be reported upon.

This work focuses on the application of C_3A for the removal of zinc from aqueous solution. The objectives of this research are: (1) to prove the possibility of zinc removal by C_3A; (2) to investigate the effect of pH, temperature and contact time on zinc uptake by C_3A; and (3) to study and discuss the potential mechanism for the removal of zinc. X-ray diffraction (XRD) and scanning electron microscope (SEM) were adopted to identify the reacting products. It was found that C_3A was a special material which could efficiently remove a large amount of Zn^{2+} (13.73 $mmol{\cdot}g^{-1}$ in practice).

2. Materials and methods

2.1. Synthesis of C_3A

C_3A was synthesized through the solid state reaction based on the report [25, 26]. The mixture of $CaCO_3$ and $Al(OH)_3$ at a molar ratio of 3:2 was heated in quartz crucibles at 1350 ^oC for 4 h, followed by two intermediate grindings. The heating process was conducted in quartz crucibles and continued until XRD (with a modified Franke test) analysis indicated that the free lime content was under 0.5%. The specific area of C_3A designated by Blaine's method was 330 m^2/kg [27], and the average crystallite size of C_3A obtained by thermal treatment at 1350 ^oC was evaluated to be 49.3 nm [28]. In the previous work [23], the morphology of C_3A demonstrated a non-rule structure with smooth edges. The chemical formula of C_3A used in this work was proved to be $Ca_{2.87}Al_2O_{5.87}$ by XRD and ICP-AES tests.

2.2. Removal of zinc

The adsorption isotherm experiment was implemented in $Zn(NO_3)_2$ solutions with different Zn^{2+} concentrations from 0.0 to 17.0 $mmol \cdot L^{-1}$. Typically, a mass of 0.02 g of C_3A was used to treat 20 mL of $Zn(NO_3)_2$ solution, and no pH adjustment or other adjustments were made to the solution (initial pH=6.5). The mixture was shaken at 150 rpm in a thermostatic bath shaker at 298 K for 16 h. After that, the supernatant was immediately filtered through a 0.45 μm membrane for complete particle removal. The resulting liquid was used to determine the residual zinc and then the adsorption capacity of tricalcium aluminate was calculated. All assays were conducted in triplicate. The effects of temperature and initial solution pH on the removal efficiency were investigated similarly, with the zinc concentration of 17.0 $mmol \cdot L^{-1}$. The pH dependence of zinc adsorption by C_3A was evaluated in batch assays at room temperature. The pH was adjusted from 3.0 to 7.0 by NaOH and HNO_3. The condition of pH>7 was not referred in this work because Zn^{2+} ions would involve in precipitation reaction in alkaline environment and form $Zn(OH)_2$ precipitates. The temperature dependence of zinc adsorption by C_3A was evaluated in thermostatic water bath with the temperature ranging from 298 to 328 K.

The adsorption kinetics experiment was performed as a function of contact time by dispersing 0.02g of C_3A in 20 mL of $Zn(NO_3)_2$ solution (17.0 $mmol \cdot L^{-1}$) at room temperature, and no pH adjustment or other adjustments were made to the solution. At

suitable time intervals, 10.0 mL of the liquid was extracted for the determination of zinc concentration. The suspended solid was collected after filtration and then dried at 343 K for 4 h for further characterization. The solid samples with different contact time of 5, 60, 120, 480, and 960 minutes were named as Zn-5, Zn-60, Zn-120, Zn-480 and Zn-960, respectively. Additionally, the concentrations of Zn^{2+}, Ca^{2+} and Al^{3+} were measured with an atomic emission spectrometer (Perkin Elmer ICP-AES, 2100DV).

2.3. Synthesis of ZnAl-NO_3-LDH

ZnAl-NO_3-LDH was prepared by co-precipitation and used for X-ray diffraction analysis. Two solutions were firstly prepared, one of which contained 0.1 mol·L^{-1} $Zn(NO_3)_2$ and 0.05 mol·L^{-1} $Al(NO_3)_3$, and the other contained 0.15 mol·L^{-1} NaOH. Then they were mixed at a volume ratio of 1:2 under vigorous stirring with a magnetic stirrer. The synthesis of ZnAl-NO_3-LDH was performed under N_2 gas atmosphere in order to prevent the influence of CO_2. The sample was vigorously stirred for 24 h, and then the precipitate was centrifuged, washed with distilled water and dried at 343 K for 4 h.

2.4. X-ray diffraction

The powder X-ray diffraction patterns for the solid samples were collected in a D/max RBX diffractometer with Cu Kα (40 kV, 100 mA) radiation at room temperature. The samples were scanned at a rate of 6 ^{o}·min^{-1} in the range of 5-65 ^{o}.

2.5. Scanning electron microscope

The morphology of samples was obtained using a scanning electron microscope (Hitachi S-4800). Samples were coated with a thin layer of evaporated gold, and the SEM images were obtained using a secondary electron detector. The electric tension was 30 kV, and the working distance was 7 mm.

3. Results and discussion

3.1. Zinc removal process

3.1.1. Adsorption isotherm

Adsorption capacity at different aqueous equilibrium concentrations (*Ce*) could be illustrated by the adsorption isotherm. The behavior of the adsorption isotherm of Zn^{2+} on C_3A at room temperature was shown in Fig. 1. The adsorbed amount of zinc

increased linearly from 0 to 11.88 mmol·g^{-1} at relatively low zinc equilibrium concentrations from 0 to 0.015 mmol·L^{-1}. Afterwards, the increasing rate slowed down and reached adsorption equilibrium when the *Ce* of Zn^{2+} was 0.173 mmol·L^{-1}. The maximum removal capacity of zinc by one gram of C_3A was 13.73 mmol, which was much higher than other kinds of adsorbents (see Supporting Information, Table 1). The equilibrium isotherm was agreed with the two equilibrium models, Langmuir model (1) and Freundlich model (2):

$$Q_e=Q_m bC_e/(1+bC_e) \quad (1)$$

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (2)$$

and the derived constants of these models were shown in table 2. The experimental results showed that the correlation coefficient for the Langmuir model (0.971) was much higher than that of the Freundlich model (0.706). This revealed that the hydrates of C_3A had homogeneous surfaces with monolayer adsorption sites for zinc. Also Langmuir indicated a limited number of sites and site saturation, and the high-energy sites with high equilibrium constant had a significantly higher affinity than low-energy sites with a low equilibrium constant [29].

3.1.2. Effect of temperature on zinc removal

As shown in Fig. 2, the zinc removal amounts by C_3A at different temperature from 298 to 328 K were13.50, 14.16, 12.62 and 11.01 mmol·g^{-1}, respectively. The results revealed that an increase in temperature from 308 to 328 K caused a decrease in the amount of zinc removed. The reason for this phenomenon was that higher temperature could accelerate the transformation process from the initial hydrates of C_3A such as C_4AH_{19} to cubic katoite phase C_3AH_6, which was the most stable calcium aluminate hydrate at room temperature [21, 30]. The temperature dependent adsorption process was associated with changes in several thermodynamic parameters such as standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of adsorption. The calculations were done by using the following Eq. (3):

$$\Delta G = -RT \ln b \quad (3)$$

where R is the universal gas constant (8.314 J/K mol); T is the absolute temperature

(K); *b is* the Langmuir constant. According to Van't Hoff model (Eq. (4)):

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

ln *b* against 1/*T* was plotted. *ΔS* could be obtained from the intercept while *ΔH* could be determined from the slope. The thermodynamic parameters obtained at four different temperatures (298-328 K) were presented in Table 3. The negative values of *ΔG* indicated the spontaneous nature of zinc adsorption. The positive value of *ΔH* indicated the endothermic nature of the adsorption process. The positive value of *ΔS* suggested the increased randomness at the solid/solution interface during the adsorption of zinc by C_3A. The amount of zinc removed at 308 K was slightly higher than that of 298 K, because the increasing temperature could result in the reduction of the system's free energy (*ΔG*) [31]. It could be deduced that an increase in the temperature from 298 to 308 K had a greater impact on the *ΔG* than that of on the transformation process of hydrates mentioned above.

3.1.3. Effect of initial solution pH on zinc removal

The amount of zinc removed by C_3A at different initial $Zn(NO_3)_2$ solution pH was determined by varying the pH between 3.0 and 7.0 (see Supporting Information, Fig. 3). It was obvious that zinc removal process was highly dependent on the pH value of solution. The removal capacity of zinc by C_3A increased with increasing pH, because alkaline environment provided more hydroxyl (OH^-), which contributed to a coagulation process with Zn^{2+} ions. Zinc adsorption was favored at pH values near 7.0 (13.82 $mmol \cdot g^{-1}$). In addition, the uptake capacity of zinc was decreased at pH 4.0 and then sharply declined to 0.33 $mmol \cdot g^{-1}$ when the pH reached 3.0. This indicated that an acidic environment adversely affected zinc uptake by C_3A, because significant LDH dissolution occurred at low pH [32]. The corresponding temperature and pH dependence of zinc removal by C_3A was summarized in table 4.

3.1.4. Adsorption kinetics

The behavior of the adsorption kinetics of Zn^{2+} by C_3A at room temperature was illustrated in Fig. 4. When the initial concentration of $Zn(NO_3)_2$ was 17.0 $mmol \cdot L^{-1}$, the removed amount of Zn^{2+} increased dramatically within the first 2 h and then

reached its maximum value. The maximum amount of zinc adsorbed by C_3A was 13.73 $mmol \cdot g^{-1}$. The kinetics data was analyzed using pseudo-first-order, pseudo-second-order and Elovich models. As shown in table 5, the zinc adsorption was better described by the pseudo-first-order kinetics:

$$Q_t = q_e(1\text{-}\exp(\text{-}k_1 t)) \quad (3)$$

where q_e is the Zn amount adsorbed on C_3A at the equilibrium (mmol Zn/g), Q_t *is* the Zn amount adsorbed at time t (mmol Zn/g), and k is the adsorption rate constant (min^{-1}). An accurate estimation of Q_t as well as the highest correlation coefficient (R^2=0.971) was achieved by using the pseudo-first-order model. This model revealed that zinc adsorption was indeed a fast process ($t_{1/2} = 0.693/k_1 = 45$ min).

3.2. Precipitant products characterization

X-ray diffraction patterns of Zn-5, Zn-60, Zn-120, Zn-480, Zn-960, as well as ZnAl-NO_3-LDH were shown in Fig. 5. It could be seen that a series of sharp reflections with high intensity such as (003), (006), (009), and (110) appeared in the XRD patterns of the resultant products, indicating relatively well-formed crystalline layered structure. The typical (003), (006), (009) and (110) peaks appeared in the XRD patterns of Zn-5 and Zn-60 were consistent with that of ZnAl-NO_3-LDH (marked with "#") synthesized in this work, and the basal spacing (0.89Å) was in accordance with that of ZnAl-NO_3-LDH as well. Moreover, the peaks of CaAl-LDH (marked with "♦") were observed at 2θ=11.22 ^{o} in the XRD patterns of Zn-5 and Zn-60. The peaks appeared to be weaker as the contact time increased from 5 to 60 min and completely disappeared at 120 min. This suggested that the hydrates of C_3A (CaAl-LDHs) involved in zinc removal process during the first two hours. As for Zn-120, Zn-480 and Zn-960, the diffraction peaks of (003), (006), (009), (015), (018) and (110) could be indexed as pure ZnAl-CO_3-LDH (marked with "*") recorded on JCPDS card 48-1023, and the presence of the reflections of (009), (015), (018) and (110) were referred to a hexagonal lattice with rhombohedral 3R symmetry [33], this structure could also be confirmed by SEM images (Fig. 6). The SEM pictures of Zn-960 revealed that the crystallites resembled approximately hexagonal plates with sharp particle edge and similar particle size, and the plates were several nanometers

thick with a lateral distance around 0.2-0.3 μm. In addition, the peaks of ZnAl-NO_3-LDH at 9.96 ^{o} appeared to be weaker as the contact time increased from 120 to 960 min, while the intensity of the reflections of ZnAl-CO_3-LDH at 11.54 ^{o} gradually became stronger. This phenomenon suggested that as the reaction time increased, nitrate anions in the interlayer region of ZnAl-LDH were gradually replaced by carbonate anions which came from the dissolved CO_2. In fact, the common anion-exchange capability for LDH increased in the following sequence: NO_3^-<Cl^-<SO_4^{2-}<CO_3^{2-} [34], and this provided an evidence for the anion exchange between NO_3^- and CO_3^{2-}. At last, the peaks of calcium-based LDH were not found in the XRD patterns of Zn-120, Zn-480 and Zn-960, which revealed that the reaction of Zn^{2+} ions and C_3A was complete.

3.3. Removal mechanism of C_3A

It is well known that Ca-based LDHs can spontaneously interact with varieties of anions, such as Cl^- [35], BrO_3^- [36] and PO_4^{3-} [37]. It has been proven that the relevant reaction mechanisms are anion exchange and self-dissolution followed by re-precipitation due to the partial dissolution of Ca-based LDHs, which are obviously different from those of other LDHs [15, 24, 38]. Therefore, to make a clear approach to describe the interacting mechanism of Ca-based LDHs and zinc, the concentrations of released Ca^{2+} and $Al(OH)_4^-$ during Zn^{2+} uptake were investigated. Indeed, it could be seen in Fig. 7 and Fig. 8, some interesting phenomenon happened during the adsorption process.

As shown in Fig. 7, it was found that when 0.02 g C_3A was added into pure water, 6.5 mmol·L^{-1} Ca^{2+} and 4.6 mmol·L^{-1} $Al(OH)_4^-$ were in this solution, and the ratio of Ca and Al was close to 3:2. Theoretically, if C_3A dissolved in the solution completely, the concentrations of released Ca^{2+} and $Al(OH)_4^-$ should be 10.9 mmol·L^{-1} and 7.4 mmol·L^{-1}, respectively. It indicated that the dissolution of C_3A occurred in water with solubility approximately 58.6%. Then, as the initial Zn^{2+} concentrations rose to 17.0 mmol·L^{-1} (i.e. saturation), the content of released Ca^{2+} gradually increased to 10.7 mmol·L^{-1} while the $Al(OH)_4^-$ reduced to almost 0.0 mmol·L^{-1}. It could be deduced that the released $Al(OH)_4^-$ ions were involved in the reaction process with Zn^{2+}, as

expressed by the following chemical equation:

$$4Zn^{2+}+2Al(OH)_4^-+4OH^-+2NO_3^-+4H_2O \rightarrow Zn_4Al_2(OH)_{12}(NO_3)_2\cdot 4H_2O. \quad (3)$$

To further verify the reaction mechanism, the solution components in the kinetics experiment with the initial concentration of zinc in saturation (17.0 $mmol\cdot L^{-1}$) were investigated and revealed in Fig. 8. It showed that the concentration of $Al(OH)_4^-$ was nearly zero all the time, which implied that all of the released $Al(OH)_4^-$ ions reacted with Zn^{2+} during zinc uptake process (Eq.(3)) and no $Al(OH)_4^-$ left at the end of the reaction. Meanwhile, the concentration of Ca^{2+} increased from 1.0 $mmol\cdot L^{-1}$ to 10.7 $mmol\cdot L^{-1}$ in the first 2 hours and then reached the saturation. It could be assumed that if Zn^{2+} removal was all attributed to the precipitation of $Al(OH)_4^-$ ions, then each $Al(OH)_4^-$ would be combined with two Zn^{2+}. Similarly, the amount of Zn^{2+} removed would be equal to the content of released Ca^{2+} if cation exchange was the only removal process. Thus, it could be easily calculated that the amount of Zn^{2+} removed would be 14.3 $mmol\cdot g^{-1}$ for precipitation model and 10.7 $mmol\cdot g^{-1}$ for cation exchange models. However, the amount of zinc removed in this work was determined to be 13.7 $mmol\cdot g^{-1}$, which meant that the cation exchange also existed in the zinc removal process, as follows:

$$Ca_4Al_2(OH)_{12}NO_3\cdot 4H_2O + 4Zn^{2+} \rightarrow Zn_4Al_2(OH)_{12}(NO_3)_2\cdot 4H_2O + 4Ca^{2+} \quad (4)$$

The existence of the cation exchange was also proved by the attenuation of the peaks represented CaAl-LDH in the XRD patterns.

Based on the analysis of the results, it could be concluded that both the precipitation and cation exchange existed in the zinc removal process. A general scheme of the reaction between zinc and C_3A was proposed (Fig. 9). During the hydration of C_3A, metastable compounds, CaAl-LDHs (e.g.C_4AH_{19} and C_2AH_8), were initially formed, producing free ions of Ca^{2+} and $Al(OH)_4^-$ in the solution. Then, the cation exchange between Zn^{2+} and Ca^{2+} on the main layers of CaAl-LDH and the precipitation process between Zn^{2+} and released $Al(OH)_4^-$ took place, leading to the formation of ZnAl-NO_3-LDH. As contact time increased, the CO_3^{2-} ions formed due to dissolved CO_2 in the solution intercalated into the interlayer of ZnAl-NO_3-LDH and resulted in the formation of ZnAl-CO_3-LDH.

4. Conclusion

From the present work, it was found that tricalcium aluminate was an excellent zinc adsorbent, which could effectively remove a large amount of Zn^{2+} from aqueous solutions in a short time. The maximum removal amount of zinc by C_3A could reach 13.73 $mmol \cdot g^{-1}$ within 2 h. The temperature and pH could influence the zinc removal process dramatically, and the highest zinc removal capacity was obtained with the initial pH of $Zn(NO_3)_2$ solution between 6.0 to 7.0 and the temperature around 308 K. The main zinc removal mechanism by C_3A was attributed to the cation exchange and precipitation. The XRD patterns revealed that the resulting product was ZnAl-NO_3-LDH initially. However, as the reaction time increased, the dissolved CO_3^{2-} could intercalate into the interlayer spacing of ZnAl-LDH and resulted in a formation of ZnAl-CO_3-LDH.

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